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Methods for Producing Heat-Resistant Oligomers

Rosilov Mansur Sirgiyevich, Qodirov Alibek Rauf o'g'li
Karshi Engineering and Economic Institute
rosilovm@mail.ru

A B S T R A C T

Despite the attractiveness of this approach in the creation of polymer parts and assemblies for structural purposes, the use of laser stereolithography is currently limited to the creation of prototypes and models of various products and assemblies.

A R T I C L E I N F O

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Despite the attractiveness of this approach for creating polymer parts and assemblies for structural purposes, at present, the use of laser stereolithography is limited only to the creation of prototypes and layouts of various products and assemblies. Obtaining finished structures based on polymers with a given architectonics by implementing the "monomer-finished product" scheme is one of the strategic directions of modern materials science. The recent increased interest in these polymers is also associated with the emerging problems of new technologies that are in need of materials that combine increased heat and heat resistance with desired optical, electrical, and other properties. It is known that the majority of high-molecular compounds of the polymerization type used in laser stereolithography,

E-mail address: info@researchparks.org
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as a rule, do not have the necessary heat and thermal stability, which significantly narrows the area of their practical application at elevated temperatures. One of the approaches to solving these problems is the radical or ionic polymerization of various monomers containing polyheteroarylenes dissolved in them. [1]. In this case, graft copolymers are formed, which differ significantly in properties from the corresponding homopolymers and their mechanical mixtures. However, in a number of cases, the glass transition temperature and thermal stability of the obtained copolymers change not so significantly, and sometimes even lead to a decrease in these characteristics. Obtaining three-dimensional cross-linked structures by radical polymerization with the participation of difunctional monomers makes it possible to achieve a significant improvement in the thermal and mechanical properties of polymer systems. In connection with the foregoing, the development of new approaches to the creation of previously unknown heat-resistant high-strength three-dimensional structures with desired properties and easy to process is one of the most important aspects of modern science. At the first stage, oligoamides and oligoimides with terminal amino groups were obtained, which were then treated with a twofold molar excess of acrylic or methacrylic acid chloride in aprotic dipolar amide solvents. The yield of reaction products in terms of the starting monomers was more than 90%.

A significant drawback of the described approaches to the preparation of oligomers with (meth)acrylamide groups is the use of hydrolytically unstable (meth)acrylic acid chlorides. In addition, during the synthesis, hydrogen chloride is released, which can cause corrosion of equipment [3]. In this regard, we have developed a new approach to the preparation of unsaturated oligomers of this type, which consists in the interaction of the terminal amino groups of oligomers with acrylic acid in the presence of N,N-dicyclohexylcarbodiimide (DCC) as a condensing agent. A preliminary study was made of a model reaction of two equivalents of acrylic acid with 4,4-diaminodiphenyl oxide (DADPO). It was found that the reaction proceeds easily at room temperature in an aprotic dipolar solvent (for example, MP) in the presence of an equivalent amount of DCC relative to acrylic acid. In this case, the model compound, that is, the model diacrylamide DADPO (DAA), is formed in almost quantitative yield within 30 min. The found optimal regime for the synthesis of a model compound (DAA) made it possible to implement this process for the modification of oligoamides and oligoimides. In both cases, the interaction proceeded in many respects similarly to the model reaction, and the reaction products were formed in more than 95% yield. Despite the attractiveness of this approach for creating polymer parts and assemblies for structural purposes, at present, the use of laser stereolithography is limited only to the creation of prototypes and mock-ups of various products and assemblies [4]. Obtaining finished structures based on polymers with a given architectonics through the implementation of the “monomer-finished product” scheme is one of the strategic directions of modern materials science. The recent increased interest in these polymers is also associated with the emerging problems of new technologies that are in need of materials that combine increased heat and heat resistance with desired optical, electrophysical, and other properties.

It is known that the majority of high-molecular compounds of the polymerization type used in laser stereolithography, as a rule, do not have the necessary heat and thermal stability, which significantly narrows the scope of their practical application at elevated temperatures. One approach to solving these problems is the radical or ionic polymerization of various monomers containing polyheteroarylenes dissolved in them. In this case, graft copolymers are formed, which differ significantly in properties from the corresponding homopolymers and their mechanical mixtures. However, in some cases, the glass transition temperature and thermal stability of the obtained copolymers do not change so significantly, and sometimes it leads to a decrease in these characteristics. [5]. Obtaining three-dimensional cross-linked structures by radical polymerization with the participation of difunctional monomers makes it possible to achieve a significant improvement in the thermal and mechanical properties of polymer systems. In connection with the foregoing, the development of new approaches to the creation of previously unknown heat-resistant high-strength three-dimensional structures with desired properties and easy to process is one of the most important aspects of modern science. Despite the attractiveness of this approach for creating polymer parts and assemblies for structural purposes, at present, the use of laser stereolithography is limited only to the creation of prototypes and layouts of various products and assemblies. Obtaining finished structures based on polymers with a given architectonics through the implementation of the scheme "monomer - finished product" is one of the strategic directions of modern materials science. The recent increased interest in these polymers is also associated with the emerging problems of new technologies that are in need of materials that combine increased heat and heat resistance with desired optical, electrical, and other properties. It is known that the majority of high-molecular compounds of the polymerization type used in laser stereolithography, as a rule, do not have the necessary heat and thermal stability, which significantly narrows the scope of their practical application at elevated temperatures. One approach to solving these problems is the radical or ionic polymerization of various monomers containing polyheteroarylenes dissolved in them. In this case, graft copolymers are formed, which differ significantly in properties from the corresponding homopolymers and their mechanical mixtures. However, in a number of cases, the glass transition temperature and thermal stability of the obtained copolymers change not so significantly, and sometimes even lead to a decrease in these characteristics. Obtaining three-dimensional cross-linked structures by radical polymerization with the participation of difunctional monomers makes it possible to achieve a significant improvement in the thermal and mechanical properties of polymer systems. In connection with the foregoing, the development of new approaches to the creation of previously unknown heat-resistant high-strength three-dimensional structures with desired properties and easy to process is one of the most important aspects of modern science.

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E-mail address: info@researchparks.org
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